

PATENT BUREAU OF JAPAN
OFFICIAL GAZETTE FOR UNEXAMINED PATENTS (A)

Japanese Patent Application Publication Kokai: Hei 7-138559

Publication Date: May 30, 1995

Number of Claims: 5

Request for Examination: Not requested (Total of 6 pages)

<u>International Class.</u>	<u>JP Class.</u>	<u>Intrabureau No.</u>	<u>FI</u>	<u>Tech. Expression</u>
C 09 K 5/00		F		
F 25 B 15/00		B		

Aqueous solution composition for use in absorption heat pumps

Application No: Hei 5-309912

Application Date: November 16, 1993

Inventors: Kikutaro Fujikura
941-1-2-206 Obomachi
Kopoku-ku
Yokohama-shi, Kanagawa-ken

Yukikazu Nishiyama
656 Yamanishi
Futamiyamachi
Naka-gun, Kanagawa-ken

Applicant: 000220262
Tokyo Gas Corp., Ltd.
5-20, 1-chome
Kaigan
Minato-ku, Tokyo-to

Agent: Hirokuni Kamo, patent attorney

[Title of the Invention]

Aqueous solution composition for use in absorption heat pumps

[Summary]

[Composition]

An aqueous solution composition containing water as the cooling medium and an iodide as the absorbing component and, in some cases, a nitrate, for use in absorption heat pump that is made of carbon steel and/or stainless steel, to which an antimony compound and a reducing agent are added.

[Effect]

In absorption heat pumps, corrosion of carbon steel and/or stainless steel, the structural materials, can be prevented over a long period of time. In particular, when the antimony compound used is antimony trioxide (Sb_2O_3) and the reducing agent is sodium bisulfite, formation of free iodine is prevented and thus corrosion of the iron materials forming the absorption heat pump can be prevented with certainty.

[Patent Claims]

[Claim 1]

An aqueous solution composition for use in absorption heat pumps, characterized by the fact that it is obtained by adding an antimony compound and a reducing agent in an aqueous solution containing water as the cooling medium and an iodide as the absorbing component for use in absorption heat pumps that are made of carbon steel and/or stainless steel.

[Claim 2]

An aqueous solution composition for use in absorption heat pumps, characterized by the fact that it is obtained by adding an antimony compound and a reducing agent in an aqueous solution containing water as the cooling medium and an iodide and a nitrate as the absorbing components for use in absorption heat pumps that are made of carbon steel and/or stainless steel.

[Claim 3]

The aqueous solution composition for use in absorption heat pumps described under Claims 1-2, characterized by the fact that the antimony compound used is antimony trioxide (Sb_2O_3) and the reducing agent is one with a higher solubility.

[Claim 4]

The aqueous solution composition for use in absorption heat pumps described under Claims 1-3, characterized by the fact that the reducing agent is sodium bisulfite (NaHSO_3).

[Claim 5]

The aqueous solution composition for use in absorption heat pumps described under Claims 1-4, characterized by the fact that the antimony compound used is antimony trioxide (Sb_2O_3) and the reducing agent is sodium bisulfite (NaHSO_3).

[Detailed Description of the Invention]

[0001]

[Field in the Industry]

The present invention relates to a working medium composition, that is, an aqueous solution composition, used in absorption heat pumps. More specifically, it relates to an aqueous solution composition containing water as the cooling medium and an iodide or and iodide and a nitrate as the absorbing component for use in absorption heat pumps that are made of carbon steel and/or stainless steel.

[0002]

[Prior Art]

Various working media have been proposed for use in absorption heat pumps. In particular, media based on combination of water and ammonia (NH_3 : cooling medium) and combination of water and halides have been in practical use.

[0003]

For the medium based on combination of water and halides, water is used as the cooling medium and the halide is mainly lithium bromide (LiBr) and lithium chloride (LiCl).

[0004]

However, for the above system consisting of water and lithium bromide, when the apparatus is small or air cooling is used, the concentration of lithium bromide has to be increased. Consequently, the lithium bromide crystallizes. Thus, it is difficult to miniaturize the apparatus or to use air cooling.

[0005]

To improve the limitation resulting from crystallization, it was proposed to add zinc bromide or zinc chloride to this aqueous solution composition consisting of water and lithium bromide. However, by adding such compounds to this solution, the solution becomes acidic, not only becoming highly corrosive but also forming a precipitate (due to the formation of zinc hydroxide) in dilute solution of about 10 wt. % or lower.

[0006]

The absorption heat pump is essentially composed of a generator, condenser, evaporator and absorber. These apparatuses are made of soft steel or other carbon steel materials and copper, copper-nickel alloy, such as cupronickel, etc., and others. Among these materials, the corrosion problem is particularly significant for the carbon steel material forming the generator that works at a high temperature. Sufficient attention has to be paid to this problem as well as to the problems of crystallization of the above absorbing components and of formation of the above precipitate. The same problem exists if the structural material is stainless steel.

[0007]

To ensure smooth operation of the absorption heat pump, it is necessary to maintain the entire system air-tight. This feature is also important for corrosion prevention. When water is used as the cooling medium and the absorbent is lithium bromide or lithium chloride, this working medium is corrosive for iron type materials, such as carbon steel, stainless steel, etc., that forms the above major components of the absorption heat pump. Thus, normally it is necessary to use corrosion inhibitors.

[0008]

As the inhibitor, the following compounds have been proposed, for example: chromates,*such as lithium chromate, etc., molybdates, such as lithium molybdate, etc., tungstates, nitrites, nitrates,azole salts, amine compounds, etc.

[0009]

In Japanese Patent Publication Kokoku Hei 5-28751, a new absorbing solution for absorption refrigerators with improvement on the limitation of crystallization, consisting mainly of water and halide, is described. According to this invention, by using lithium bromide, lithium iodide, lithium chloride and lithium nitrate as the components at specific blend ratios in water, the crystallization temperatures are, for example, 0.5°C and 1.9°C at concentrations of the components of 63.6 wt% and 62.0 wt%, respectively.

[0010]

Nevertheless, when this new working medium is used, sufficient attention still needs to be paid to corrosion prevention. For instance, in Japanese Patent Application Publication Kokai Hei 1-174588, it is noted that "aqueous solution of a lithium halide including lithium iodide" is particularly corrosive, and measures against the action of such solution are also described.

[0011]

According to that invention, the traditional problem, namely, that the use of the inhibitors alone is not sufficient to suppress corrosion, could be solved by adding an antimony compound, in particular antimony trioxide.

[0012]

The mechanisms for the action of the antimony compound were suggested to be (1) the reduction of liberated halogen to its ion and the inhibition of the formation of free halogen, and (2) that the antimony compound is adsorbed on the surface of the copper and steel materials of the machine, forming a tight protection layer thereby preventing the elution of iron and steel.

[0013]

Lithium iodide is used as a component because of the characteristics of lithium iodide itself. During the operation of a heat pump using this compound, it is necessary to inhibit the formation of free halogen, but not to convert the liberated halogen to the original ion. Furthermore, the inhibition is preferably complete.

[0014]

Against the above background, the inventors have been studying various aqueous solution compositions proposed for use in absorption heat pumps using carbon steel and/or stainless steel as structural materials, containing water as the cooling medium and halides including iodides, such as lithium iodide, etc., as the absorbent. They noticed that when an antimony compound is used as the inhibitor, formation of free iodine occurs, and if a nitrate is present, the formation of free iodine progresses even more significantly.

[0015]

They made this observation in Practical Examples 1-4, shown in Table 1 under the Practical Examples section (those examples are equivalent to the comparative examples in the present invention). Firstly, in Practical Examples 1-2, a solution was prepared from 306 g of water, 261 g of LiBr, 258 g of LiI, 153 g of LiCl, totaling 878 g. To this solution, 2400 mg of LiOH and 100 mg of Sb_2O_3 (Practical Example 1) or Sb_2O_3 (Practical Example 2) were added to obtain appropriate test solutions.

[0016]

Each of the test solutions was placed in an emptied titanium container that was also used in the practical examples of the present invention as described below, and the container was filled with nitrogen gas and then sealed (without metal strip). The solution was maintained at 160°C for 1000 hours. After the temperature returned to room temperature, the solution was analyzed. In Practical Example 1, the solution was in the oxidized state (0.0005 N). The test metal strip was examined visually. It was found that a black layer was formed on the surface, and signs of pitting were noted.

[0017]

On the other hand, in Practical Example 2, after 1000 hours at 160°C, the solution remained in reduced state (0.0020 N). Similarly, test metal strip was examined visually. Formation of a black layer on the surface was found, but no signs of pitting were recognized.

[0018]

Subsequently, a solution containing nitrate was prepared from 306 g of water, 222 g of LiBr, 258 g of LiI, 144 g of LiCl and 44 g of LiNO₃, totaling 874 g. To this solution, 2400 mg of LiOH and 100 mg of Sb₂O₅ (Practical Example 3) or Sb₂O₃ (Practical Example 4) were added to obtain appropriate test solutions.

[0019]

Each of the test solutions was tested as in Practical Example 1 or 2. After 1000 hours, the solution was analyzed after the temperature returned to room temperature. In Practical Example 1, the solution was in the oxidized state (0.0055 N). The test metal strip was examined visually. It was found that a black layer was formed on the surface, and signs of pitting were recognized. In Practical Example 4, the solution was also in the oxidized state (0.0030 N). Similarly, the test metal strip was examined visually. A black layer was formed on the surface and signs of pitting were noted.

[0020]

Thus, in Practical Example 2, where no nitrate (LiNO₃) was used in the aqueous solution, the use of the inhibitor Sb₂O₃ was effective to some degree, whereas when nitrate (LiNO₃) was used in the aqueous solution, there was limitation to the use of Sb₂O₃.

[0021]

The reason was considered to be that although the antimony compound Sb₂O₃ itself has reducing activity, the reducing activity can not be maintained over a long period of time because of its very low solubility in aqueous solvents (it is almost insoluble in water).

[0022]

Regarding the antimony compound, Sb₂O₃, its use in large excess instead of other more soluble reducing agents that were under consideration previously. Nevertheless, a

suspension of a large amount of insoluble material in the system is not desirable, since it results in accumulation at the bottom of the container and causes corrosion subsequently.

[0023]

The inventors carried out further studies, based on these results, of the use of antimony compounds as inhibitors. As a result, they found that in this case, to prevent formation of free iodine, it is necessary to use a reducing agent even when an antimony compound (Sb_2O_3) is used. The present invention has thus been achieved.

[0024]

[Problems to be Solved by the Invention]

The objective is to provide an aqueous solution composition containing water as the cooling medium and an iodide as the absorbing component and, in some cases, a nitrate, for use in absorption heat pumps that are made of carbon steel and/or stainless steel, in which the formation of free iodine is essentially completely inhibited so that corrosion of ferrous materials can be prevented and the above described problems can be solved.

[0025]

[Means of Solving the Problems]

The present invention provides an aqueous solution composition containing water as the cooling medium and an iodide as the absorbing component for use in absorption heat pumps that are made of carbon steel and/or stainless steel, to which an antimony compound and a reducing agent are added.

[0026]

Moreover, the present invention provides an aqueous solution composition containing water as the cooling medium and an iodide and a nitrate as the absorbing components for use in absorption heat pumps that are made of carbon steel and/or stainless steel, to which an antimony compound and a reducing agent are added. Here, "absorption heat pumps" is a generalized term. It includes refrigerators.

[0027]

The antimony compound can be antimony pentoxide (Sb_2O_5), antimony trioxide (Sb_2O_3), etc. When antimony trioxide (Sb_2O_3) is used, the reducing agent used is preferably

a compound with a solubility higher than that of the antimony compound. In the present invention, it is particularly preferable to use sodium bisulfite (sodium hydrogen sulfite: NaHSO_3) as the reducing agent in combination with antimony trioxide (Sb_2O_3) as the antimony compound.

[0028]

In the present invention, it was found that among various reducing agents, the use of sodium bisulfite (sodium hydrogen sulfite: NaHSO_3) is the most effective. This reducing agent, in the presence of an antimony compound as the inhibitor, inhibits the formation of free iodine so that corrosion of the carbon steel and/or stainless steel materials can be prevented over a long period of time.

[0029]

The inhibitor and the reducing agent added to the aqueous solution composition for the absorption heat pump are gradually consumed over a long period of time of operation of the absorption heat pump. In this particular aspect, sodium bisulfite is preferable since it is relatively more easily soluble in the aqueous solution composition. The amount of addition can be up to its solubility in the particular aqueous solution in which it is used. It can be appropriately determined based on the amounts of iodide and nitrate (if any), etc.

[0030]

In the present invention, the "aqueous solution composition containing water as the cooling medium and an iodide as the absorbing component" and "aqueous solution composition containing water as the cooling medium and an iodide and a nitrate as the absorbing components" can be a water-lithium iodide system, water-lithium bromide-lithium iodide system, water-lithium iodide-lithium nitrate system, lithium bromide-lithium iodide-lithium chloride-lithium nitrate system, etc.

[0031]

[Practical Examples]

In the following, a practical example of the present invention is described in comparison with the above practical examples (Comparative Examples). Nevertheless, the present invention is not to be limited to this practical example.

A solution composition (about 500 mL) was prepared as shown in Table 1. On the other hand, 5 test metal sheets, 2 mm thick, 30 mm wide and 50 mm long, were prepared from carbon steel. The material used for the test metal sheets was equivalent to JIS G 3131-1990.

[0032]

Then, the above aqueous solution was placed in an emptied titanium container with an internal volume of 1 L (1 liter). The above 5 test metal sheets were suspended in the solution, and then the container was sealed. A vacuum pump was used to remove the air, then nitrogen gas was introduced to atmospheric pressure. The container was then heated to a specific temperature.

[0033] is the table, which is at the end of the text. - Translator

[0034]

The internal temperature of the container was maintained at 160°C (the accuracy of temperature control was within 1°C) for 1000 hours. Then heating was stopped, and when the temperature returned to room temperature, the container was opened. The aqueous solution was analyzed (the oxidized or reduced state was determined by iodine titration), and the surface of the test sheet was examined. The results are shown in Table 1.

[0035]

As shown, in Practical Example 1 where Sb_2O_5 was used as the antimony compound (corresponding to Test Example 1), after treatment at 160°C for 1000 hours, the solution remained in the reduced state (0.038 N), and on the surface of the test sheet a tight black layer was formed without any sign of pitting. In Practical Example 2 similar results were obtained in these aspects.

[0036]

In Practical Example 3 where lithium nitrate was included and antimony trioxide (Sb_2O_3) was used as the inhibitor, after the treatment under the same conditions for 1000 hours, the solution remained in a strongly reduced state (0.035 N), and on the surface of the test sheet a tight black layer was formed without any signs of pitting. Compared to Test Example 3 without using sodium bisulfite where the solution was in the oxidized state

(0.0030 N) and the formed surface layer was not tight and with signs of pitting, the above effect was clear.

[0037]

[Effect of the Invention]

As described above, by the present invention, an aqueous solution composition containing water as the cooling medium and an iodide as the absorbing component for use in absorption heat pumps that are made of carbon steel and/or stainless steel, to which an antimony compound and a reducing agent are added, can be obtained, and thus by its use, corrosion of the carbon steel and/or stainless steel materials can be prevented over a long period of time.

[0038]

Moreover, the same effect also can be obtained when both iodide and nitrate are included in the composition. In particular, by using antimony trioxide (Sb_2O_3) as the inhibitor and sodium bisulfite as the reducing agent, the formation of free iodine and hence corrosion of the iron type metal materials forming the absorption heat pump can be prevented with certainty.

Table 1

Example No.	solution composition (g)	additive (mg)			heating temperature (°C)	heating time (h)	oxidized or reduced state of the solution		state of the test sheet surface
		LiOH	Sb compound	reducing agent			before heating (N)	after heating (N)	
Test Example 1	water: 306 LiBr: 261 LiI ₂ : 258 LiCl: 53	2400	Sb ₂ O ₃ 100	0	180	1000	0.0000	oxidized state 0.0005	black surface layer with signs of pitting
Pract. Example 1		"	"	NaHSO ₃ 1000	"	"	reduced state 0.038	reduced state 0.038	tight black surface layer, without signs of pitting
Test Example 2		"	Sb ₂ O ₃ 100	0	"	"	reduced state 0.0025	reduced state 0.0020	black surface layer, without signs of pitting
Test Example 3	water: 306 LiBr: 222 LiI ₂ : 258 LiCl: 44 LiNO ₃ : 44	2400	Sb ₂ O ₆ 100	0	"	"	0.0000	oxidized state 0.0055	black surface layer, with signs of pitting
Practical Example 2		"	"	NaHSO ₃ 1000	"	"	reduced state 0.038	reduced state 0.0030	tight black surface layer, without signs of pitting
Practical Example 4		"	Sb ₂ O ₃ 100	0	"	"	reduced state 0.0025	oxidized state 0.0030	black surface layer, with signs of pitting
Practical Example 3		"	"	NaHSO ₃ 1000	"	"	reduced state 0.041	reduced state 0.035	tight black surface layer, without signs of pitting